PB84-200914

Wastes from Manufacture of Dyes and Pigments. Volume 5. Diphenylmethane and Triarylmethane Dyes and Pigments

SRI International, Menlo Park, CA

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Jun 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-200914

EPA-600/2-84-111e
June 1984

WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 5. DIPHENYLMETHANE AND TRIARYLMETHANE DYES AND PIGMENTS

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Contract 68-03-2944
Task 1, Subtask 4

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-84-111e		PB84 200914

4. TITLE AND SUBTITLE	5. REPORT DATE
WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOL. 5: DIPHENYLMETHANE AND TRIARYLMETHANE DYES AND PIGMENTS	June 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Julia E. Gwinn & David C. Bomberger	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Ave. Menlo Park, CA 94025	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. 68-03-2944
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Office of Research & Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A preliminary study of the manufacture of Diphenylmethane and Triarylmethane dyes was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced and the known U.S. producers.

The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and five companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	47
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

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ABSTRACT

A preliminary study of the manufacture of Diphenylmethane and Triarylmethane dyes was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced and the known U.S. producers.

The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and five companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This report is submitted in fulfillment of contract No. 68-03-2944 by SRI International under the sponsorship of the U.S. Environmental Protection agency. The report covers the period December 1981 to August 1982, and work was completed as of July 31, 1983.

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SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes are listed in regulations as being hazardous because of their chemical composition. The objective of this study was to determine if wastes produced by the manufacture of dyes and pigments in the United States require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing is used to identify all wastes that may contain significant chemical hazards. An analysis of the industry is used to determine specific manufacturers where the candidate wastes may be produced. This information allows contractors of the U.S. Environmental Protection Agency to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes produced from the manufacture of diphenylmethane and triarylmethane dyes and pigments.

The diphenylmethane and triarylmethane dyes and pigments are among the oldest synthetic dyes. They give dyeings of extreme brightness and purity, but their fastness properties, particularly to light, are quite poor. Despite their light fugitiveness, these dyes and pigments are widely used because of their brilliant shades, their extremely high tinctorial values, and their relative low cost. In 1972, production of 4000 metric tons for all triarylmethane dyes (this figure includes diphenylmethane dyes) was reported to the U.S. Tariff Commission (1974). This represents 3.4% of the total reported U.S. dye production of 120,000 metric tons for that year. Diphenylmethane and triarylmethane dyes (and pigments) represented the fourth largest structural class of dyes based on U.S. production volume. Data on U.S. production by structural class have not been reported since 1972; therefore it is not possible to determine from public sources whether the relative importance and/or total production of these dyes and pigments has changed.

Table 1 gives 1979 U.S. production data for the 48 commercially significant diphenylmethane and triarylmethane dyes and pigments included in this study--dyes produced at greater than 2.3 metric tons and pigments produced at greater than 0.5 metric tons. Table 1 is arrainged according to the Colour Index (C.I.) number (Colour Index, The Society of Dyers and Colourists, 1980). These 1979 U.S. production levels were taken from the

Table 1

DIPHENYLMETHANE AND TRIARYLMETHANE DYES
AND PIGMENTS INCLUDED IN THIS STUDY

C.I. No.	C. I. Name	1979 U.S. Commercial Production (metric tons)
41000	Basic Yellow 2	> 4.5
41001	Basic Yellow 37	> 2.3
42000	Basic Green 4	> 6.8
42000:1	Solvent Green 1	> 4.5
42000:2	Pigment Green 4, fugitive[a]	> 0.9
42000:2	Pigment Green 4, PTA[b]	> 0.5
42025	Basic Blue 1	> 6.8
42025[c]	Basic Blue 2	> 2.3
42025:1	Pigment Blue 9	> 0.9
42040	Basic Green 1	> 2.3
42040:1	Pigment Green 1	2.7
42040:1/ 49005:1[d]	Pigment Green 2, fugitive[a]	> 0.5
42040:1/ 49005:1[d]	Pigment Green 2, PMA[b]	> 1.4
42040:1/ 49005:1[d]	Pigment Green 2, PTA[b]	8.2
42053	Food Green 3	> 2.3
42080	Acid Blue 7	> 2.3
42085	Acid Green 3	> 2.3
42090	Food Blue 2/Acid Blue 9[e]	126
42090	Acid Blue 9	> 9.1
42090:1	Pigment Blue 24	> 1.4
42095	Acid Green 5	> 2.3
42140	Basic Blue 5	> 2.3
42510:2	Pigment Violet 4	> 0.5
42535	Basic Violet 1	763
42535:1	Solvent Violet 8	> 4.5

Table 1 (Continued)

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons)
42535:2	Pigment Violet 3, fugitive[a]	90
42535:2	Pigment Violet 3, PMA[b]	175
42535:2	Pigment Violet 3, PTA[b]	9.5
42555	Basic Violet 3	> 6.8
42555:1	Solvent Violet 9	> 2.3
42595	Basic Blue 7	> 6.8
42595:1	Solvent Blue 5	> 2.3
42595:2	Pigment Blue 1, PMA[b]	40
42595:2	Pigment Blue 1, PTA[b]	> 0.9
42600	Basic Violet 4	> 2.3
42600:1	Pigment Blue 14	> 1.4
42640	Acid Violet 49	> 4.5
42735	Acid Blue 104	> 2.3
42750:1	Pigment Blue 19	> 0.5
42760	Solvent Blue 23	> 2.3
42775	Solvent Blue 3	> 4.5
44025	Acid Green 16	> 2.3
44040	Basic Blue 11	> 2.3
44040:2	Pigment Blue 10	> 0.5
44045	Basic Blue 26	> 4.5
44045:1	Solvent Blue 4	> 6.8
44045:2	Pigment Blue 2	> 0.5
--	Basic Blue 77	> 2.3

[a]The fugitive or nonpermanent pigments based on cationic dyes are usually produced by precipitation with tannic acid and tartar emetic (antimony potassium tartrate), or with synthetic organic precipitants. Sometimes clay, fatty acids, or rosin soaps are used as precipitants.

[b]The permanent basic dye pigments are produced by the precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA), phosphomolybdic acid (PMA), and phosphotungstomolybdic acid (PTMA).

[c]According to Colour Index, C.I. Basic Blue 2 is "very similar" to C.I. 42025.

Table 1 (Concluded)

[d]C.I. Pigment Green 2 is composed of the triphenylmethane pigment C.I. 42040:1 (C.I. Pigment Green 1) and the thiazole pigment C.I. 49005:1 (C.I. Pigment Yellow 18).

[e]The dye C.I. 42090 is known as C.I. Food Blue 2 and C.I. Acid Blue 9. Some manufacturers producing C.I. Food Blue 2, also market it as the dye C.I. Acid Blue 9. Some manufacturers produce only the dye of a quality to be marketed as the C.I. Acid Blue 9.

Organic Dyes and Pigments Data Base prepared by SRI International (Swett et al., 1983). For 28 dyes and 12 pigments the production is shown only as an amount greater than a minimum number. These are dyes and pigments produced by fewer than three manufacturers or by three or more where one or two dominate the market. Public sources do not list specific production amounts in these cases. Production data are for the commercial product, which may include solvents, other diluents, and impurities in addition to the specific dye chemical of interest; concentration of the organic dye in the commercial product may vary from 10% to 100%. No information was reported to the U.S. Tariff Commission concerning the concentration of the dye in the commercial product.

Two dyes and six pigments of the 48 dyes and pigments listed in Table 1 have a known 1979 U.S. commercial production volume. These dyes (all of the triarylmethane class) are listed in Table 2, arranged according to their production volume. These eight substances represent a combined 1979 U.S. commercial production of about 1,200 metric tons.

In the following sections of this report the process chemistry of diphenylmethane and triarylmethane dyes and pigments is discussed. Sources of wastes during dye and pigment manufacture are discussed in detail.

Table 2

TRIARYLMETHANE DYES AND PIGMENTS OF KNOWN 1979 U.S. COMMERCIAL PRODUCTION

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons)
42535	Basic Violet 1	763
42535:2	Pigment Violet 3, PMA[a]	175
42090	Food Blue 2/Acid Blue 9[b]	126
42535:2	Pigment Violet 3, fugitive[c]	90
42595:2	Pigment Blue 1, PMA[a]	40
42535:2	Pigment Violet 3, PTA[a]	9.5
42040:1/ 49005:1[d]	Pigment Green 2, PTA[a]	8.2
42040:1	Pigment Green 1	2.7

[a]The permanent basic dye pigments are produced by the precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA), phosphomolybdic acid (PMA), and phosphotungstomolybdic acid (PTMA).

[b]The dye C.I. 42090 is known as C.I. Food Blue 2 and C.I. Acid Blue 9. Some manufacturers producing C.I. Food Blue 2 also market it as the dye C.I. Acid Blue 9. Some manufacturers produce only the dye of a quality to be marketed as the C.I. Acid Blue 9.

[c]The fugitive or nonpermanent pigments based on cationic dyes are usually precipitated with tannic acid or tartar emetic (antimony potassium tartrate), or with synthetic organic precipitants. Sometimes clay, fatty acids, or rosin soaps are used as precipitants.

[d]C.I. Pigment Green 2 is composed of the triphenylmethane pigment C.I. 42040:1 (C.I. Pigment Green 1) and the thiazole pigment C.I. 49005:1 (C.I. Pigment Yellow 18).

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of diphenylmethane and triarylmethane dye and pigment production, several waste streams were identified that might contain hazardous materials:

- Discarded shipping containers. These would contain dye and pigment intermediates.
- Solid residues from process synthesis, distillation, and filtration. These would contain unreacted dye and pigment intermediates, reaction by-products, and heavy metals such as lead, copper, iron, zinc, and chromium.
- Gaseous emissions that may contain phosgene, formaldehyde, nitrogen oxides, arylamines, and other potentially hazardous materials.
- Process wastewater that may contain mother liquors from filtering operations. These may contain organic materials and heavy metals from the syntheses.
- Wastewater treatment solids. The solids may be contaminated with low levels of all the dye and pigment intermediates as well as the dyes and pigments themselves and some reaction by-products.

The information on the producers of the dyes and pigments and the materials used in the syntheses contained in Section 5 (Tables 6 and 8) was analyzed to choose a few representative manufacturers where a sampling program might be conducted to determine the composition of the waste emissions. The following companies are recommended:

American Cyanamid Co.
Dye Specialties, Inc.
H. Kohnstamm & Co., Inc.
Max Marx Color & Chemical Co.
Sterling Drug, Inc., Hilton Davis Chemical Co. Div.

The five companies recommended for a sampling program should yield samples from facilities using different manufacturing and waste treatment practices. Since there is some overlap in the dyes and pigments they produce, the five company sampling program increases the chances of identifying material in the waste streams from manufacturing the same dye or pigment that may be sensitive to plant practices.

SECTION 3

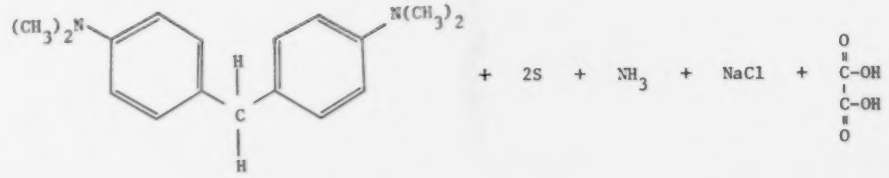
PROCESS CHEMISTRY

INTRODUCTION

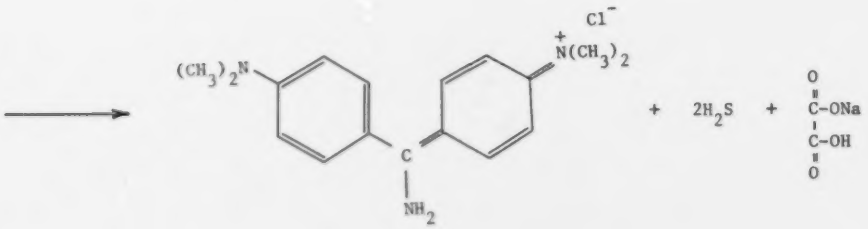
A discussion of the production of diphenylmethane and triarylmethane dyes and pigments is necessary to identify the emission sources and wastes that might be hazardous. This section focuses on the chemistry of the dye and pigment synthesis, with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products.

DIPHENYLMETHANE DYES

The diphenylmethane dyes are usually classed with the triarylmethane dyes. There are only two important commercial dyes of this class, C.I. Basic Yellows 2 and 37 (C.I 41000 and C.I. 41001, respectively). C.I. Basic Yellow 2, also known as Auramine O, is obtained by passing ammonia over a mixture of 4,4´ -bis(dimethylamino)diphenylmethane (Michler's base), sulfur, oxalic acid, and salt at a temperature that is gradually raised from 125°C to 170°C, and converting the resulting dye base into its quaternary chloride (BIOS, 1945b):



Michler's base



C.I. Basic Yellow 2
C.I. 41000

The Colour Index (The Society of Dyers and Colourists, 1980) lists as a process route the original method of heating 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) with ammonium chloride and zinc chloride at 150°C to 160°C. However, according to Abrahart (1977), this is not an economic method.

C.I Basic Yellow 37 is the ethyl analog of C.I. Basic Yellow 2 and is prepared similarly using 4,4′-bis(diethylamino)diphenylmethane rather than Michler's base.

According to Steadman et al. (1977), the manufacture of the diphenylmethane dyes is a single-step process in which formaldehyde and a dialkylaniline are mixed in the reaction vessel with the sulfur, oxalic acid, sodium chloride, and ammonia. In this condensation the Michler's base (or its ethyl analog) is first formed, then the dye is formed.

TRIARYLMETHANE DYES

The triarylmethane dyes are characterized by a central carbon atom joined to three aromatic rings. The dyes are salts of amino or hydroxy derivatives of triphenylmethane and its homologues. Only di- and tri-substituted derivatives are of commercial value, and the amino or hydroxyl groups are always in different rings in the para postions with respect to the methane carbon atom (Allen, 1971).

The triarylmethane dyes are very similar in their general chemical reactions. The reactions shown in Figure 1 of the red triaminotriarylmethane dye pararosaniline are typical of the whole class (Allen, 1971; Krahler, 1955). N-Methylation and N-phenylation of the rosanilines and pararosanilines gives some very important dyes, as is discussed later.

The leuco base, as shown in Figure 1, is often produced in the dye syntheses. This leuco base is then converted to the required product. As a carbinol base, the dye is useful in solvent dye applications. Pigments may also be manufactured from the cationic dyes by converting them into insoluble tannates or by using clay or tartar emetic (antimony potassium tartrate) substrates. However, these products are restricted by their low light fastness and are known as fugitive pigments. It was discovered that improved light fastness could be obtained with complex acid precipitants such as phosphotungstic and phosphomolybdic acids (PTA and PMA, respectively) or their salts (Allen, 1971 and 1955).

Preparation of Diaminotriarylmethanes

C.I. Basic Green 4 (C.I. 42000), also known as Malachite Green, is typical of the diamino derivatives of triphenylmethane. As is shown in Figure 2, this dye is obtained by refluxing benzaldehyde (which provides one aromatic ring and the central carbon atom) with an excess of N,N-dimethylaniline in the presence of hydrochloric or sulfuric acid at 100°C for 24 hours (Allen,

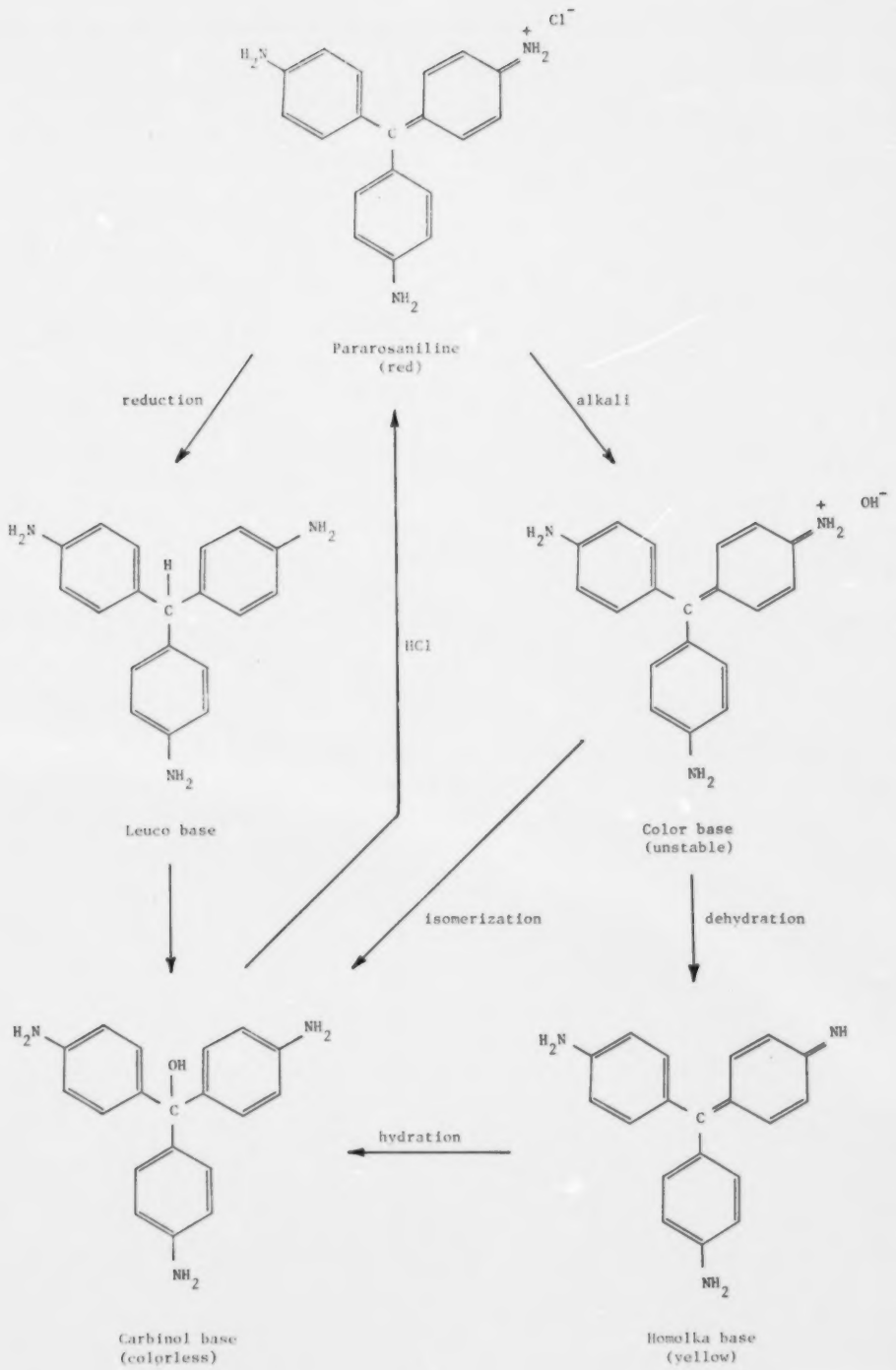
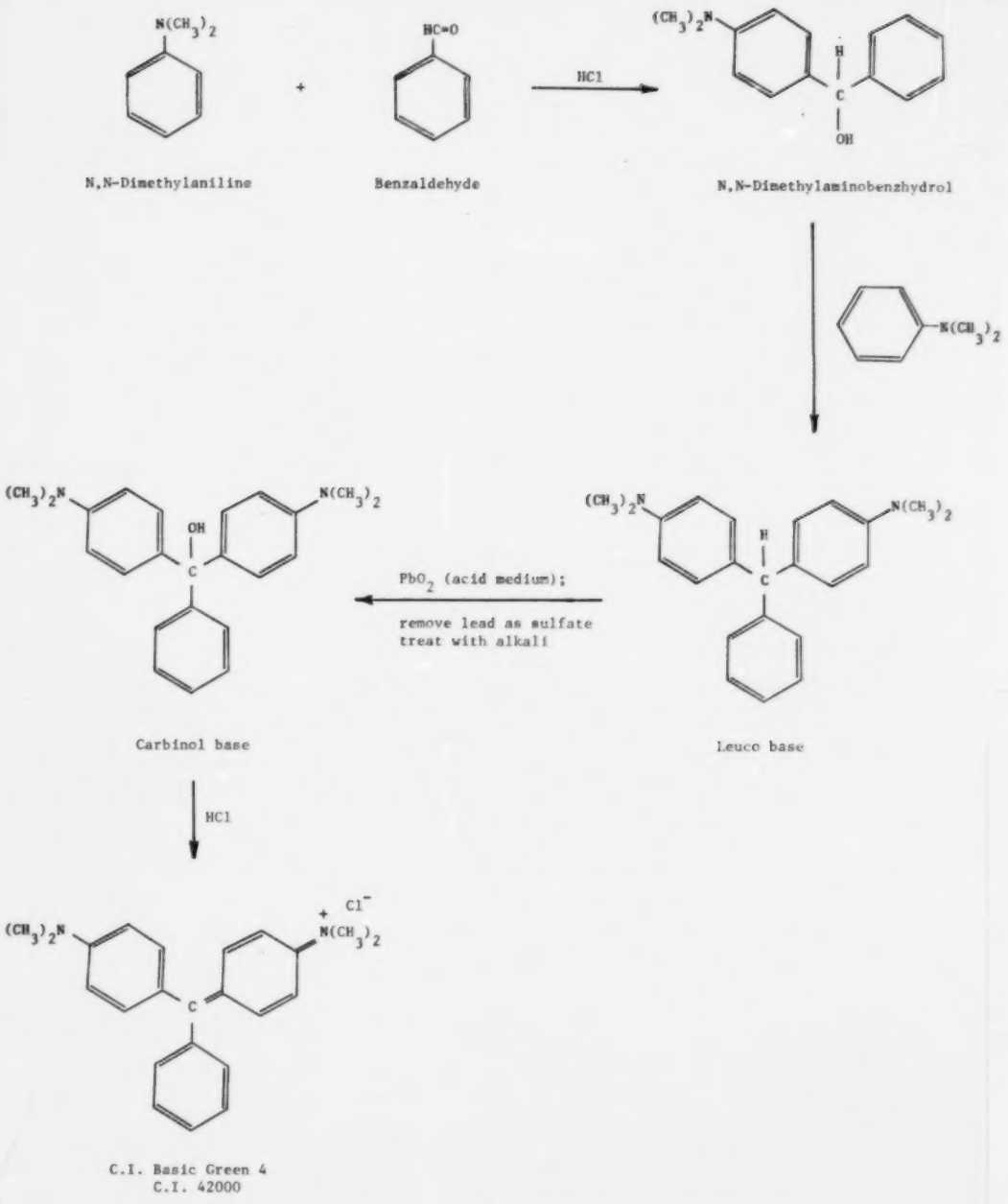


FIGURE 1 TYPICAL CHEMICAL REACTIONS OF THE TRIARYLMETHANE DYES AS TYPIFIED BY PARAROSANILINE



C.I. Basic Green 4
C.I. 42000

FIGURE 2 CHEMICAL REACTIONS USED TO PRODUCE MALACHITE GREEN

1971). According to Venkataraman (1952), 1 mole of benzaldehyde is condensed with 2.5 to 2.75 moles of dimethylaniline (which must be free of monomethylaniline). The excess of dimethylaniline ensures that all of the more expensive benzaldehyde reacts. Venkataraman reports about two-thirds mole of the acid per mole of benzaldehyde gives optimum results. After the reaction is complete, the mixture is made alkaline and the excess dimethylaniline removed by steam distillation. The residual leuco base is dissolved in ice-cold hydrochloric and acetic acids and oxidized with lead peroxide to the carbinol base. The lead is precipitated with sodium sulfate and the carbinol base converted into the quaternary chloride.

The ethyl analog of Malachite Green is Brilliant Green, C.I. Basic Green 1 (C.I. 42040), which is obtained by starting with N,N-diethylaniline and benzaldehyde.

C.I. Basic Blue 1 (C.I. 42025) is obtained by conducting similar reactions with o-chlorobenzaldehyde and N,N-dimethylaniline.

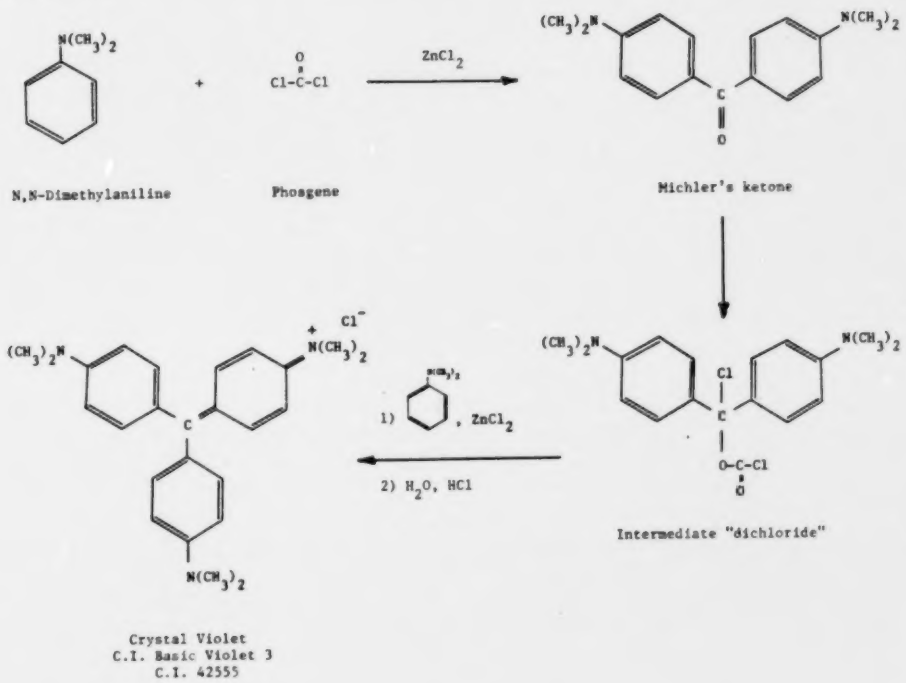
C.I Food Blue 2, also known as C.I. Acid Blue 9 (C.I. 42090), is a very important diaminotriarylmethane. In 1979, 126 metric tons were commercially produced in the United States (Table 2). This dye is the result of the condensation of o-formylbenzenesulfonic acid with α-(N-ethylanilino)-m-toluenesulfonic acid followed by oxidation, precipitation, and filtration.

Sometimes the condensation reaction is followed by a sulfonation of the leuco dye, which is then oxidized and converted to the sodium salt. Examples of dyes made by this manufacturing route are C.I. Food Green 3 (C.I. 42053) and C.I. Acid Green 5 (C.I. 42095).

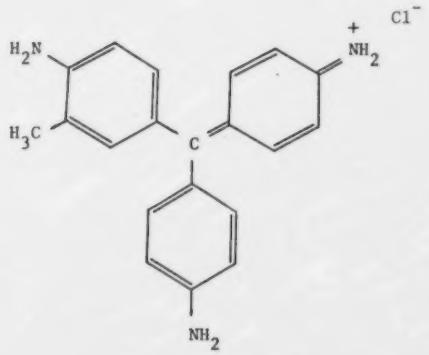
Preparation of Triaminotriarylmethanes

The single most important triarylmethane dye is the triamino derivative known as Methyl Violet, C.I. Basic Violet 1 (C.I. 42535), which had a 1979 U.S. commercial production of 763 metric tons. The pigment from this dye, C.I. Pigment Violet 3 (C.I. 42535:2), had a 1979 U.S. commercial production of 274.5 metric tons (combining the volumes for the three forms of the pigment: PMA, PTA, and fugitive). Allen (1971) describes the synthesis process as follows: N,N-dimethylaniline is first oxidized with copper sulfate in the presence of common salt and phenol. In the first reaction stage one methyl group is removed from a molecule of dimethylaniline with the formation of formaldehyde and N-methylaniline. The formaldehyde then condenses with two molecules of unchanged N,N-dimethylaniline, yielding 4,4'-bis(dimethylamino)diphenylmethane (Michler's base), which is oxidized in air to the corresponding carbinol base. Condensation between the carbinol and the N-methylaniline formed in the first stage yields the required triphenylmethane leuco base. Oxidation and acidification of the base, as shown in Figure 1 for pararosaniline, yield the chloride salt form of the dye. Note, however, that many other reactions are occurring. The dye product is actually a mixture of the chlorides of the more highly methylated pararosanilines, containing principally the N-tetra-, N-penta-, and N-hexamethyl derivatives.

The phosgene process is a useful preparation method for triamino-triarylmethanes. The dye Crystal Violet, also known as C.I. Basic Violet 3 (C.I. 42555), is obtained by reacting N,N-dimethylaniline with phosgene in the presence of zinc chloride to give 4,4'-bis(dimethylamino)benzophenone (Michler's ketone), which is further condensed with dimethylaniline to yield the dye Crystal Violet.



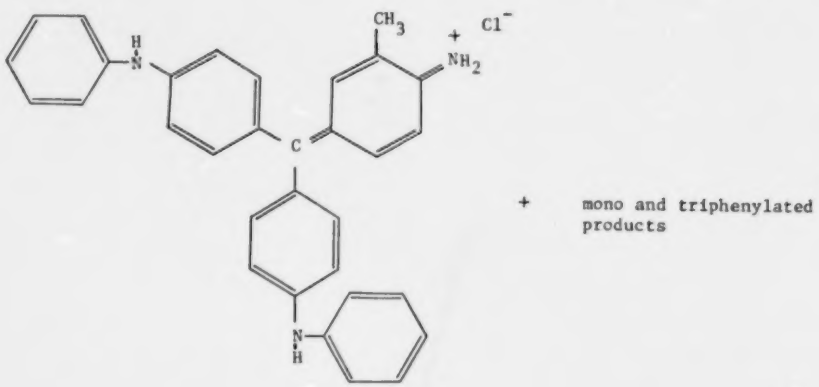
The formaldehyde process for producing triarylmethanes is illustrated by the synthesis of Magenta, C.I. Basic Violet 14 (C.I. 42510):



Magenta
C.I. Basic Violet 14
C.I. 42510

Magenta is an important triarylmethane that is often used as an intermediate in the production of other triarylmethane dyes and pigments such as C.I. Pigment Blue 19 (C.I. 42750:1) and C.I. Solvent Blue 3 (C.I. 42775). A mixture of aniline and its hydrochloride with o-toluidine, p-toluidine, and their respective hydrochlorides is reacted with formaldehyde in the presence of iron and an oxidizing agent such as nitrobenzene or arsenic acid. The carbinol base formed is then converted into the quaternary chloride.

C.I. Solvent Blue 3 (C.I. 42775) is produced via the Spirit Blue process in which Magenta is heated with an excess of aniline in the presence of benzoic acid. The degree of phenylation is controlled by a carefully defined heating schedule during the fusion (Krahler, 1955).



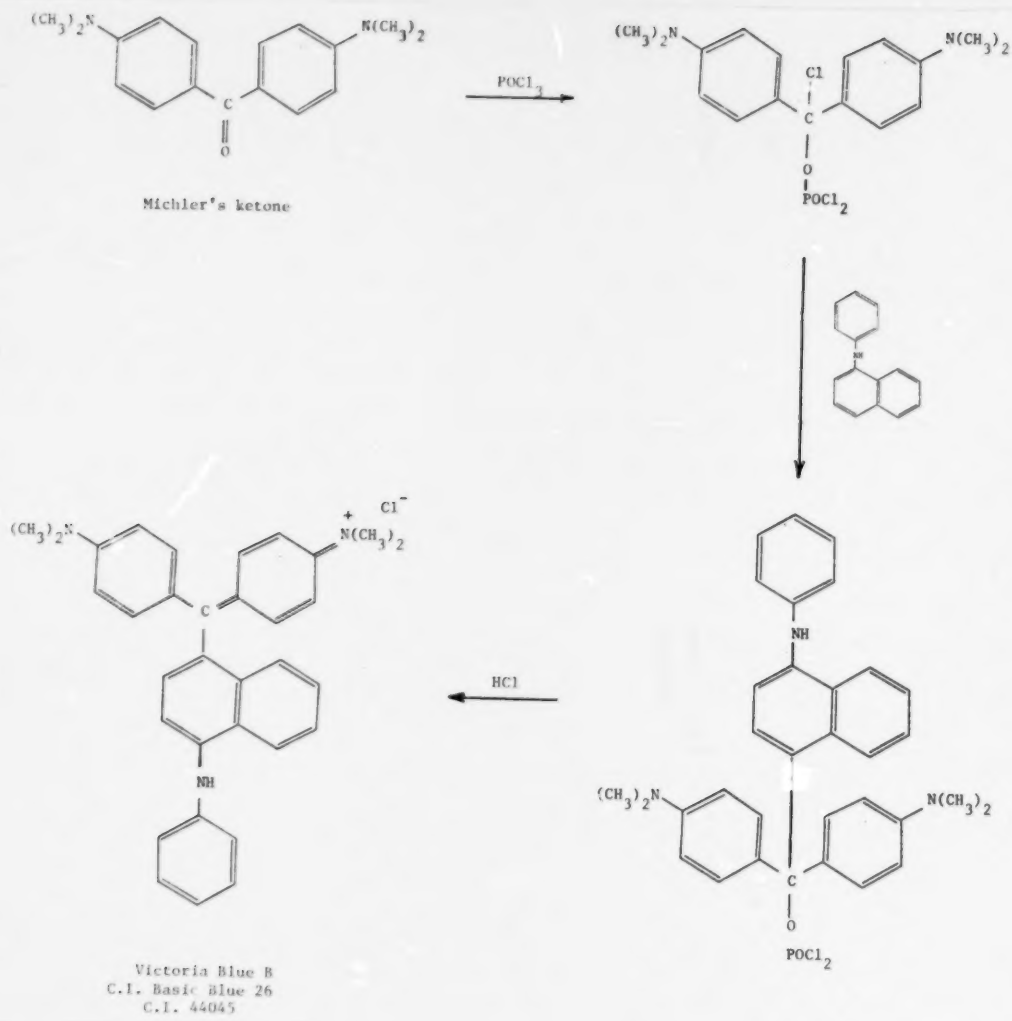
C.I. Solvent Blue 3
C.I. 42775

Preparation of Aminohydroxytriarylmethanes

The syntheses of these dyes follow common triarylmethane routes: condensation (hydroxybenzaldehyde with an aromatic amine), sulfonation (if necessary), and oxidation to the dye. C.I. Food Green 3 (C.I. 42053) is the product of p-hydroxybenzaldehyde-o-sulfonic acid with α -(N-ethylanilino)-m-toluenesulfonic acid.

Preparation of Diphenylnaphthylmethanes

A series of very valuable blue dyes are obtained by replacing one of the alkylaniline residues in N-alkyl rosanilines by an N-alkylphenylnaphthylamine or N-phenylnaphthylamine. These dyes are known as the Victoria Blues. One such dye, C.I. Basic Blue 26 (C.I. 44045), Victoria Blue B, is produced by condensing Michler's ketone with N-phenyl-1-naphthylamine in the presence of phosphorus oxychloride:



Steadman et al. (1977) report the production of the Victoria Blues as requiring two successive process steps. In the synthesis of C.I. Basic Blue 26 (C.I. 44045), N,N-dimethylaniline and formaldehyde are condensed and oxidized in the presence of sulfuric acid and sodium dichromate to form an intermediate benzhydrol. Then N-phenyl-1-naphthylamine is added along with sulfuric acid, sodium nitrite, sodium dichromate and water for condensation, nitrosation, oxidation, and hydrolysis. Steadman et al. report that noxious gas emissions from the manufacture of these dyes and pigments will always consist of nitrogen oxides and small amounts of formaldehyde.

C.I. Pigment Blue 1 (C.I. 42595:2) is an important triarylmethane pigment (see Table 2) that is derived from Victoria Pure Blue BO (C.I. Basic Blue 7, C.I. 42595). The dye is the result of condensation of the ethyl analog of Michler's ketone with N-ethyl-1-naphthylamine in toluene in the presence of phosphorus oxychloride. The pigment is precipitated out of the dye solution with phosphomolybdic acid (PMA) or phosphotungstic acid (PTA).

SECTION 4

ORGANIC AND INORGANIC INTERMEDIATES AND REAGENTS IN DIPHENYLMETHANE AND TRIARYLMETHANE DYES AND PIGMENT PRODUCTION

Information on the organic and inorganic intermediates and reagents used to produce the diphenylmethane and triarylmethane dyes and pigments listed in Table 1 was compiled from information in the Colour Index (The Society of Dyers and Colourists, 1980), BIOS Reports 1433 and 1482, and Steadman et al. (1977). Only one dye listed in Table 1, C.I. Basic Blue 77, is of unknown chemical structure, and therefore no process information was available.

Table 3 lists the organic intermediates, Table 4 lists the organic reagents, and Table 5 lists the inorganic reagents used in the production of the dyes and pigments listed in Table 1. Tables 3, 4, and 5 also identify those substances which, if present in solid wastes, are subject to regulation as hazardous wastes under RCRA (Federal Register, 1980). These substances are identified by their hazard code.

Table 3

ORGANIC INTERMEDIATES USED TO PRODUCE DIPHENYLMETHANE AND TRIARYLMETHANE DYES AND PIGMENTS

Organic Intermediates	Hazardous Waste Listing[a]
Aniline	T
_____, N,N-diethyl-	
_____, N,N-dimethyl-	
Aniline hydrochloride	
Benzaldehyde	
_____, o-chloro-	
_____, p-diethylamino-	
_____, p-dimethylamino-	
Benzaldehyde-o-sulfonic acid, p-hydroxy-	
Benzenedisulfonic acid, 4-formyl-m-	
Benzenesulfonic acid, p-amino- (Sulfanilic acid)	
_____, o-formyl-	
Benzhydrol, 4,4′-bis(dimethylamino)-	
Benzoic acid	
Benzophenone, 4,4′-bis(diethylamino)-	
_____, 4,4′-bis(dimethylamino)- (Michler's ketone)	
Benzylamine, N-ethyl-N-phenyl-	
p,p′-(Dichloromethylene)bis[N,N-dimethylaniline]	
Diphenylmethane,4,4′-bis(diethylamino)-	
_____, 4,4′-bis-(dimethylamino)- (Michler's base)	
_____, p,p′-diamino- (p,p′-Methylenedianiline)	
Formaldehyde	T
Methane, tetrachloro- (Carbon tetrachloride)	T
Methanol	T

Table 3 (Concluded)

Organic Intermediates	Hazardous Waste Listing[a]
2,7-Naphthalenedisulfonic acid	
1-Naphthylamine, N-ethyl-	
_____, N-phenyl-	
Phosgene	H,T
Sodium acetate	
Toluene, α,α,α-trichloro-	
m-Toluenesulfonic acid, α-(N-ethylanilino)-	
_____, α-(N-ethyl-m-toluidino)-	
Toluidine, o-	
_____, p-	
_____, N-ethyl-o-	
Toluidine hydrochloride, o-	T
_____, p-	

[a] Hazard codes from the Federal Register (1980), indicate the basis for EPA listing the material hazardous: Acute Hazardous (H), Ignitable (I), and Toxic (T).

Table 4

ORGANIC REAGENTS USED TO PRODUCE
DIPHENYLMETHANE AND TRIARYLMETHANE
DYES AND PIGMENTS

Organic Reagents	Hazardous Waste Listing[a]
Acetic acid	
Antimony potassium tartrate	T
Nitrobenzene	I,T
o-Nitrotoluene	
Oxalic acid	
Phenol	T
Quebracho extract	
Toluene	T

[a]Hazard codes from the Federal Register, (1980) indicate the basis for EPA listing the material hazardous: Ignitable (I) and Toxic (T).

Table 5

INORGANIC REAGENTS USED TO PRODUCE DIPHENYLMETHANE AND TRIARYLMETHANE DYES AND PIGMENTS

	Hazardous Waste Listing[a]
Ammonia	
Ammonium chloride	
Ammonium hydroxide	
Arsenic acid	EP, H,T
Copper sulfate	
Cupric chloride	
Ferric chloride	
Ferrous chloride	
Hydrochloric acid	
Hydrogen sulfide	
Lead peroxide	EP, T
Lead sulfate	EP, T
Oleum	
Phosphomolybdic acid	
Phosphorus oxychloride	
Phosphotungstic acid	
Sodium carbonate	
Sodium chloride	
Sodium dichromate	EP
Sodium hydroxide	
Sodium nitrate	
Sodium sulfide	
Sulfur	
Zinc chloride	

[a]Hazard codes from the Federal Register (1980) indicate the basis for EPA listing the material hazardous: EP Toxic (EP), Acute Hazardous (H), and Toxic (T).

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, the most significant material losses are intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from dye manufacturing are present either in the product or in the solid waste streams regulated under RCRA, which include wastewater, solid residues, and the vapor and dust emissions. The material in the wastewater is discharged in the plant effluent (although some is destroyed by treatment as described below), and some is discharged on wastewater treatment solids.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 3 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. The dye manufacturing equipment required to produce triarylmethane and diphenylmethane dyes and pigments consists of well-stirred batch reactors (steel and glass-lined) and standard filter presses, grinders, dryers, and blenders (Steadman et al., 1977).

The dyes or pigments are usually produced in batches, and the plants typically contain several reactor trains. Complex dyes and pigments may require use of several reactor trains. Production of colors is usually rotated by set schedules from light- to-dark colored dyes to minimize the impact of dye carry-over from multiple use of the equipment.

The diphenylmethane dyes are produced in a single process operation by condensing the organic constituents selected, as described in Section 3. The production of triarylmethane dyes may require several process operations. Often the syntheses include a filtration step to recover the desired intermediate. This intermediate is then reacted with other intermediates and reagents. All the dyes are precipitated out of the reaction mixture as a salt and filtered from the mother liquors.

Pigments produced from these cationic dyes are (1) the result of either precipitation with tartar emetic (antimony potassium tartrate) or clay or quebracho extract to yield the fugitive form or (2) the result of precipitation with the complex acids PMA or PTA to yield the more permanent pigment.

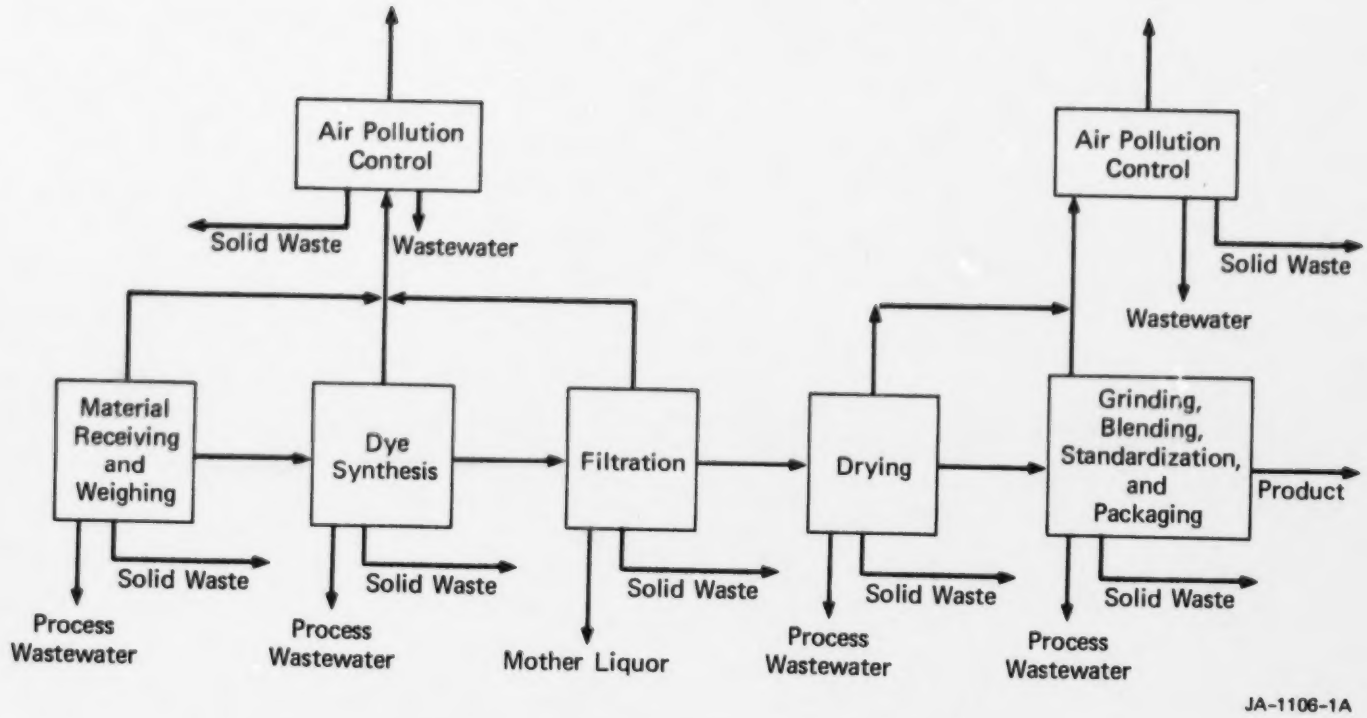


FIGURE 3 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

No information was found concerning the concentration of the dyes in the commercial products. It is believed the concentrations of the basic and acidic dyes range from 20% to 50%. Solvent dyes are generally 100% dye, but sometimes a diluent is added to standardize color.

The sources of wastes from dye manufacture identified in Figure 3 are summarized below:

- Material handling--Air emissions from raw material dusting and volatilization, solid residues on shipping containers, and process wastewaters from equipment washdown.
- Dye syntheses--Air emissions from the volatilization of intermediates and by-products from reaction vessels, solid residues from distillation residues and spills, and process wastewaters from equipment washdown.
- Product and intermediate filtration--Air emissions from unreacted intermediate and by-product volatilization during material handling, solid residues from spills, and process wastewater from equipment washdown. A significant additional source of process wastewater is the mother liquor.
- Drying--Air emissions from volatilization of by-products and unreacted intermediates in the drying oven, and solid residues from spills and dusting of the product dye.
- Grinding, blending, standardization, and packaging--Solid residues from dusts produced by the grinding operations that may be in either the air streams from vent systems designed to prevent the material from entering the workplace environment or in the solid residue from spills.
- Air pollution control--Solid residues from baghouses or scrubbers collecting fine dusts and process wastewater from scrubbers.

MATERIAL IN THE WASTE STREAMS FROM DIPHENYLMETHANE AND TRIARYLMETHANE DYE AND PIGMENT PRODUCTION

Previous studies (Lapp et al., 1979; Bomberger and Boughton, 1983) have demonstrated that the major potential source of emissions is the process wastewater, primarily because it contains the mother liquor.

On the basis of the chemistry discussed in Section 3, these mother liquors will probably contain unreacted intermediates, reaction by-products, unprecipitated dye or pigment, and salt. They may also contain mineral acids, such as sulfuric and hydrochloric acids, and organic acids, such as acetic and oxalic acids.

Table 6 lists the known intermediates and other organic chemicals used in the production of the diphenylmethane and triarylmethane dyes and pigments listed in Table 1. Some of the inorganic chemicals used in the production are

also included in the listing. Table 6 does not identify or quantify process chemistry by-products that are likely to be present, for example, isomers of required intermediates and the reaction products of these with the other intermediates and reagents used in the process. The by-products were not included in this study because very little useful information dealing with the amount or nature of these by-products was found. Table 7 gives the full names of the producers associated with the letter codes in Table 6. Table 8 lists all the producers of diphenylmethane and triarylmethane dyes and pigments and lists the dyes and pigments they manufacture.

The identity and corporate ownership of the producers is based on 1979 information. Since then, several dye production facilities or dye lines were sold. Sales that were announced in trade journals are shown as footnotes to Tables 7 and 8. A systematic search was not made to verify that all such sales have been listed, so the tables may not be complete.

Significant sources of hazardous wastes are highlighted in the following discussion.

The lead ion introduced in oxidizing leuco bases to the dye is precipitated as lead sulfate, a solid residual product. These dyes are identified in Table 6.

Another significant solid residual waste is the distillation residue in the manufacture of dyes and their corresponding pigments. These residues may contain alkylamines, arylamines, formaldehyde, and other potential hazardous wastes. Information from Steadman et al. (1977) indicates that the dyes listed below will produce a distillation residue in their manufacture:

C.I. Name	C.I. No.
Basic Green 4	42000
Basic Violet 3	42555
Basic Violet 4	42600
Acid Violet 49	42640
Basic Blue 11	44040
Basic Blue 26	44045

Manufacture of the dyes and pigments listed below will include the production of sludges containing "large amounts" of heavy metals--copper, zinc, and/or iron (Steadman et al., 1977):

C.I. Name	C.I. No.
Pigment Violet 4	42510:2
Basic Violet 1	42535
Basic Violet 3	42555
Basic Blue 7	42595
Basic Violet 4	42600
Pigment Blue 19	42750:1
Solvent Blue 23	42760
Solvent Blue 3	42775

The largest known produced triarylmethane dye and the corresponding pigment, C.I. Basic Violet 1 and C. I. Pigment Violet 3 (C.I. 42535 and C.I. 42535:2), are included in this list.

The processes identified in Table 6 that include the use of sodium dichromate could lead to chromium in the sludges produced in the manufacture.

The manufacture of triarylmethane and diphenylmethane dyes includes the production of some potentially hazardous gaseous emissions. The processes that include the use of phosgene, as identified in Section 3, are indicated in Table 6. The hydrogen sulfide formed in the production of the diphenylmethanes is usually recovered as sodium sulfide for use as a reducing agent in manufacturing other dyes. Steadman et al. (1977) report that the manufacture of the Victoria Blue dyes and pigments might result in gaseous emissions that include nitrogen oxides and small amounts of formaldehyde. Steadman et al. (1977) also report that the manufacture of the largest volume triarylmethane dye and pigment, C.I. Basic Violet 1 (C.I. 42535) and C..I. Pigment Violet 3 (C.I. 42535:2), via an air oxidation produces a gaseous emission that "could contain significant and hazardous amounts of toxic arylamines."

Table 6 also identifies the processes in which formaldehyde is used. Any gaseous emissions that contain formaldehyde would presumably be scrubbed in an air pollution control system.

Most of the liquid effluents will be brines containing small amounts of organic materials. Some of the process wastewaters could be contaminated with heavy metals (copper, zinc, iron, and/or chromium). Synthesis of pigments that use tartar emetic as a precipitant may produce liquid effluents containing antimony.

The hazardous materials phenol, toluene, methanol, and tetrachloromethane are also used in the manufacture of triarylmethane dyes. The processes in which they are used are identified in Table 6. Waste streams from the manufacture of these dyes may contain these materials.

Arsenic acid is included in the list of potential reagents used in the manufacture of triarylmethane dyes (C.I. 42750:1, C.I. 42760, and C.I. 42775). It is possible to use nitrobenzene instead of arsenic acid.

The manufacture of four triarylmethane dyes (C.I. 42510:2, C.I. 42750:1, C.I. 42760, and C.I. 42775) requires the hazardous materials aniline and o-toluidine hydrochloride. The waste streams from the manufacture of these dyes may include these materials.

N-Ethyl-1-naphthylamine is used in the manufacture of C.I. Basic Blue 7, C.I. Solvent Blue 5, and C.I. Pigment Blue 1 (C.I. 42595, C.I. 42595:1, and C.I. 42595:2, respectively) and C.I. Basic Blue 11 and C.I. Pigment Blue 10 (C.I. 44040 and C.I. 44040:1, respectively). N-Phenyl-1-naphthylamine is used in the production of C.I. Basic Blue 26, C.I. Solvent Blue 4, and C.I. Pigment Blue 2 (C.I. 44045, C.I. 44045:1, and C.I. 44045:2, respectively). These dyes and pigments are highlighted because the hazardous by-product 1-naphthylamine may be produced during their manufacture.

EFFECT OF TRIARYLMETHANE DYES ON WASTEWATER TREATMENT PROCESSES

Each dye producer may have a different wastewater treatment system. Some producers discharge all process wastewaters directly into sewers and thus to publicly owned treatment works. Some producers have on-site wastewater treatment plants. All these treatment plants will be site-specific designs with site-specific behavior. Several examples of on-site treatment facilities at dye production sites have been discussed (Bomberger and Boughton, 1983; Gwinn and Bomberger, 1983).

Hunter (1973) found that two triarylmethane dyes, C.I. Basic Violet 1 (C.I. 42535 and C.I. Basic Green 4 (C.I. 42000), showed an inhibitory effect on the aerobic wastewater bacteria of an activated sludge system. Acclimation studies showed no improvement in this inhibition. Similarly, Brown et al. (1981) found that five of eight tested triarylmethane dyes showed an inhibitory effect on aerobic wastewater bacteria. They recommended that more studies be conducted to determine the consequences of significant quantities of the basic dyes reaching a sewage treatment plant.

The studies of Hunter (1973) and Brown et al. (1981) indicate there is a good chance the aerobic treatment units of many wastewater treatment facilities will not degrade the basic dyes and perhaps their intermediates. Unreacted dye molecules may remain on the wastewater solids. In some facilities, this sludge is further treated in anaerobic digesters. In other facilities the solids are transported to a landfill where they are placed in an anaerobic environment. Etzel and Grady (1973) studied the effects of two triarylmethane dyes on the anaerobic digestion of primary sewage sludge in controlled laboratory digesters. They found C.I. Basic Violet 1 (C.I. 42535) had an initial inhibitory effect that was overcome by acclimation. C.I. Basic Green 4 (C.I. 42000) had no inhibitory effect.

Table 6

ORGANIC AND INORGANIC MATERIALS THAT MAY APPEAR IN THE WASTE STREAMS FROM THE PRODUCTION OF DIPHENYLMETHANE AND TRIARYLMETHANE DYES AND PIGMENTS

(Common inorganics such as sodium chloride and hydrochloric or sulfuric acid are not included)

1979 U.S Commercial Producers	C.I. No.	C.I. Name	1979 US. Commercial Production (metric tons/yr)	Materials Released to the Environment
ACY LVR	41000	Basic Yellow 2	> 4.5	Basic Yellow 2 Acetic acid p-Aminobenzenesulfonic acid (Sulfanilic acid) 4,4'-Bis(dimethylamino)benzophenone (Michler's ketone) 4,4'-Bis(dimethylamino)diphenylmethane (Michler's base) N,N-Dimethylaniline Formaldehyde Oxalic acid
ACY	41001	Basic Yellow 37	> 2.3	Basic Yellow 37 p-Aminobenzenesulfonic acid (Sulfanilic acid) 4,4'-Bis(dimethylamino)diphenylmethane (Michler's base) N,N-Diethylaniline Formaldehyde
ACY BAS DSC	42000	Basic Green 4	> 6.8	Basic Green 4 Benzaldehyde N,N-Dimethylaniline α,α,α-Trichlorotoluene Lead peroxide Lead sulfate
ACY DSC	42000:1	Solvent Green 1	> 4.5	Solvent Green 1 Benzaldehyde N,N-Dimethylaniline α,α,α-Trichlorotoluene Lead peroxide Lead sulfate
MRX UHL	42000:2	Pigment Green 4, fugitive[a]	> 0.9	Pigment Green 4 Benzaldehyde N,N-Dimethylaniline α,α,α-Trichlorotoluene Lead peroxide Lead sulfate Antimony potassium tartrate
ACY	42000:2	Pigment Green 4, PTA[b]	> 0.5	Pigment Green 4 Benzaldehyde N,N-Dimethylaniline α,α,α-Trichlorotoluene Lead peroxide Lead sulfate
BAS DSC SDH	42025	Basic Blue 1	> 6.8	Basic Blue 1 o-Chlorobenzaldehyde N,N-Dimethylaniline Lead peroxide Lead sulfate

Table 6 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 US. Commercial Production (metric tons/yr)	Materials Released to the Environment
DSC	42025[c]	Basic Blue 2	> 2.3	Basic Blue 2 Unknown
LVR	42025:1	Pigment Blue 9	> 0.9	Pigment Blue 9 o-Chlorobenzaldehyde N,N-Dimethylaniline Lead peroxide Lead sulfate
DSC	42040	Basic Greeen 1	> 2.3	Basic Green 1 Benzaldehyde N,N-Diethylaniline Lead peroxide Lead sulfate
KON LVR MRX UHL	42040:1	Pigment Green 1	2.7	Pigment Green 1 Benzaldehyde N,N-Diethylaniline Lead peroxide Lead sulfate
UHL	42040:1/ 49005:1[d]	Pigment Green 2, fugitive[a]	> 0.5	Pigment Green 2 Pigment Green 1 Pigment Yellow 18 Benzaldehyde N,N-Diethylaniline Methanol p-Toluidine Lead peroxide Lead sulfate Antimony potassium tartrate
KON MRX UHL	42040:1/ 49005:1[d]	Pigment Green 2, PMA[b]	> 1.4	Pigment Green 2 Pigment Green 1 Pigment Yellow 18 N,N-Diethylaniline Methanol p-Toluidine Lead peroxide Lead sulfate
ACY KON MRX UHL	42040:1/ 49005:1[d]	Pigment Green 2 PTA[b]	8.2	Pigment Green 2 Pigment Green 1 Pigment Yellow 18 Benzaldehyde N,N-Diethylaniline Methanol p-Toluidine Lead peroxide Lead sulfate
WJ	42053	Food Green 3	> 2.3	Food Green 3 α-(N-Ethylanilino)-m-toluenesulfonic acid p-Hydroxybenzaldehyde-o-sulfonic acid
SDH	42080	Acid Blue 7	> 2.3	Acid Blue 7 N-Ethyl-N-phenylbenzylamine 4-Formyl-m-benzenedisulfonic acid Oxalic acid Sodium dichromate

Table 6 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 US Commercial Production (metric tons/yr)	Materials Released to the Environment
TRC	42085	Acid Green 3	> 2.3	Acid Green 3 Benzaldehyde α-(N-Ethylanilino)-m-toluenesulfonic acid Lead peroxide Lead sulfate
BCC KON SDH WJ	42090	Food Blue 2/Acid Blue 9[e]	126	Food Blue 2/Acid Blue 9 α-(N-Ethylanilino)-m-toluenesulfonic acid o-Formylbenzenesulfonic acid Oxalic acid Sodium dichromate
BAS LVR WJ	42090	Acid Blue 9	> 9.1	Acid Blue 9 α-(N-Ethylanilino)-m-toluenesulfonic acid o-Formylbenzenesulfonic acid Oxalic acid Sodium dichromate
BOR KON SDH	42090:1	Pigment Blue 24	> 1.4	Pigment Blue 24 α-(N-Ethylanilino)-m-toluenesulfonic acid o-Formylbenzenesulfonic acid Oxalic acid Sodium dichromate
WJ	42095	Acid Green 5	> 2.3	Acid Green 5 Benzaldehyde N-Ethyl-N-phenylbenzylamine
DSC	42140	Basic Blue 5	> 2.3	Basic Blue 5 o-Chlorobenzaldehyde N-Ethyl-o-toluidine
KCW	42510:2	Pigment Violet 4	> 0.5	Pigment Violet 4 Aniline Aniline hydrochloride Nitrobenzene o-Toluidine o-Toluidine hydrochloride p-Toluidine p-Toluidine hydrochloride
ACY BAS BCC DSC	42535	Basic Violet 1	763	Basic Violet 1 N,N-Dimethylaniline Formaldehyde Phenol
ACY DSC	42535:1	Solvent Violet 8	> 4.5	Solvent Violet B N,N-Dimethylaniline Formaldehyde Phenol
ACY BAS KCW KON MGR UHL	42535:2	Pigment Violet 3, fugitive[a]	90	Pigment Violet 3 N,N-Dimethylaniline Formaldehyde Phenol Antimony potassium tartrate

Table 6 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 US Commercial Production (metric tons/yr)	Materials Released to the Environment
BAS DUP KON MGR MRX SDH UHL	42535:2	Pigment Violet 3, PMA[b]	175	Pigment Violet 3 N,N-Dimethylaniline Formaldehyde Phenol
ACY BAS KON MRX UHL	42535:2	Pigment Violet 3, PTA[b]	9.5	Pigment Violet 3 N,N-Dimethylaniline Formaldehyde Phenol
DSC DUP SDH	42555	Basic Violet 3	> 6.8	Basic Violet 3 4,4´-Bis(dimethylamino)benzhydrol 4,4´-Bis(dimethylamino)benzophenone (Michler's ketone) N,N-Dimethylaniline Phosgene
DSC	42555:1	Solvent Violet 9	> 2.3	Solvent Violet 9 4,4´-Bis(dimethylamino)benzhydrol 4,4´-Bis(dimethylamino)benzophenone (Michler's ketone) N,N-Dimethylaniline Phosgene
DSC DUP SDH	42595	Basic Blue 7	> 6.8	Basic Blue 7 4,4´-Bis(diethylamino)benzophenone N,N-Diethylaniline N-Ethyl-1-naphthylamine Phosgene Toluene
DSC	42595:1	Solvent Blue 5	> 2.3	Solvent Blue 5 4,4´-Bis(diethylamino)benzophenone N,N-Diethylaniline N-Ethyl-1-naphthylamine Phosgene Toluene
BNS CGY KON MGR MRX UHL	42595:2	Pigment Blue 1, PMA[b]	40	Pigment Blue 1 4,4´-Bis(diethylamino)benzophenone N,N-Diethylaniline N-Ethyl-1-naphthylamine Phosgene Toluene
MRX SDH	42595:2	Pigment Blue 1, PTA[b]	> 0.9	Pigment Blue 1 4,4´-Bis(diethylamino)benzophenone N,N-Diethylaniline N-Ethyl-1-naphthylamine Phosgene Toluene

Table 6 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 US Commercial Production (metric tons/yr)	Materials Released to the Environment
DSC	42600	Basic Violet 4	> 2.3	Basic Violet 4 N,N-Diethylaniline Phosgene
BAS DUP LVR	42600:1	Pigment Blue 14	> 1.4	Pigment Blue 14 N,N-Diethylaniline Phosgene
SDH TRC	42640	Acid Violet 49	> 4.5	Acid Violet 49 Dimethylaminobenzaldehyde N,N-Dimethylaniline α-(N-Ethylanilino)-m-toluenesulfonic acid Formaldehyde
ATL	42735	Acid Blue 104	> 2.3	Acid Blue 104 p-Diethylaminobenzaldehyde α-(N-ethyl-m-toluidino)-m-toluene-sulfonic acid Dichromate-oxalic acid
SW	42750:1	Pigment Blue 19	> 0.5	Pigment Blue 19 Basic Violet 14 Solvent Blue 3 Aniline Aniline hydrochloride Benzoic acid Nitrobenzene o-Nitrotoluene o-Toluidine o-Toluidine hydrochloride p-Toluidine p-Toluidine hydrochloride
BAS	42760	Solvent Blue 23	> 2.3	Solvent Blue 23 Basic Red 9 Aniline Aniline hydrochloride Benzoic acid p,p´-Diaminodiphenylmethane Nitrobenzene Tetrachloromethane (Carbon tetrachloride) p-Toluidine p-Toluidine hydrochloride Arsenic acid
ACY SW	42775	Solvent Blue 3	> 4.5	Solvent Blue 3 Basic Violet 14 Acetic acid Aniline Aniline hydrochloride Benzoic acid Nitrobenzene o-Nitrotoluene Sodium acetate o-Toluidine o-Toluidine hydrochloride p-Toluidine p-Toluidine hydrochloride Arsenic acid

Table 6 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 US. Commercial Production (metric tons/yr)	Materials Released to the Environment
TRC	44025	Acid Green 16	> 2.3	Acid Green 16 4,4´-Bis(dimethylamino)benzhydrol Diethylaniline Formaldehyde 2,7-Naphthalenedisulfonic acid Lead peroxide Lead sulfate
SDH	44040	Basic Blue 11	> 2.3	Basic Blue 11 4,4´-Bis(dimethylamino)benzhydrol p,p´-(Dichloromethylene)bis [N,N-dimethyl-aniline] Dimethylaniline N-Ethyl-1-naphthylamine Formaldehyde Sodium dichromate
SDH	44040:2	Pigment Blue 10	> 0.5	Pigment Blue 10 4,4´-Bis(dimethylamino)benzhydrol p,p´-(Dichloromethylene)bis [N,N-dimethyl-aniline] Dimethylaniline N-Ethyl-1-naphthylamine Formaldehyde Sodium dichromate
DSC SDH	44045	Basic Blue 26	> 4.5	Basic Blue 26 4,4´-Bis(dimethylamino)benzhydrol p,p´-(Dichloromethylene)bis [N,N-dimethyl-aniline] Dimethylaniline Formaldehyde N-Phenyl-1-naphthylamine Sodium dichromate
DSC DUP SDH	44045:1	Solvent Blue 4	> 6.8	Solvent Blue 4 4,4´-Bis(dimethylamino)benzhydrol p,p´-(Dichloromethylene)bis [N,N-dimethyl-aniline] Dimethylaniline Formaldehyde N-Phenyl-1-naphthylamine Sodium dichromate
LVR	44045:2	Pigment Blue 2	> 0.5	Pigment Blue 2 4,4´-Bis(dimethylamino)benzhydrol p,p´-(Dichloromethylene)bis [N,N-dimethyl-aniline] Dimethylaniline Formaldehyde N-Phenyl-1-naphthylamine Sodium dichromate

Table 6 (Concluded)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 US Commercial Production (metric tons/yr)	Materials Released to the Environment
DUP	–	Basic Blue 77	> 2.3	Basic Blue 77 Unknown

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[a]The fugitive or nonpermanent pigments based on cationic dyes are usually produced by precipitation with tannic acid and tartar emetic (antimony potassium tartrate), or with synthetic organic precipitants. Sometimes clay, fatty acids, or resin soaps are used as precipitants.

[b]The permanent basic dye pigments are produced by the precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA), phosphomolybdic acid (PMA), and phosphotungstomolybdic acid (PTMA).

[c]According to Colour Index, C.I. Basic Blue 2 is "very similar" to C.I. 42025.

[d]C.I. Pigment Green 2 is composed of the triphenylmethane pigment C.I. 42040:1 (C.I. Pigment Green 1) and the thiazole pigment C.I. 49005:1 (C.I. Pigment Yellow 18).

[e]The dye C.I. 42090 is known as C.I. Food Blue 2 and C.I. Acid Blue 9. Some manufacturers producing C.I. Food Blue 2 also market it as the dye C.I. Acid Blue 9. Some manufacturers produce only the dye of a quality to be marketed as the C.I. Acid Blue 9.

Table 7

DIRECTORY OF DYE AND ORGANIC PIGMENT MANUFACTURERS, 1979

Names of manufacturers that reported production and/or sales of diphenylmethane and triarylmethane dyes and pigments to the U.S. International Trade Commission for 1979 are listed below in order of their identification codes as used in Table 6.

Code	Name of Company	Code	Name of Company
Dye Manufacturers			
ACY	American Cyanamid Co.	KON	H. Kohnstamm & Co., Inc.
ATL	Atlantic Chemical Corp.	LVR	C. Lever Co., Inc.
BAS	BASF Wyandotte Corp.	SDH	Sterling Drug, Inc., Hilton Davis Chemical Co. Div.
BCC	Buffalo Color Corp.	TRC	Toms River Chemical Corp.
DSC	Dye Specialties, Inc.		
DUP	E. I. duPont de Nemours[a] & Co., Inc.	WJ	Werner-Jenkinson Co.
Pigment Manufacturers			
ACY	American Cyanamid Co.	KON	H. Kohnstamm & Co., Inc.
BAS	BASF Wyandotte Corp.	LVR	C. Lever Co., Inc.
BOR	Borden, Inc., Printing Ink Div., Pigments Div.	MGR	Magruder Color Co., Inc.
BNS	Binney and Smith, Inc.	MRX	Max Marx Color & Chemical Co.
CGY	Ciba-Geigy Corp.	SDH	Sterling Drug, Inc., Hilton Davis Chemical Co. Div.
DUP	E. I. duPont de Nemours & Co., Inc.	SW	Sherwin-Williams Co.
KCW	Keystone Color Works, Inc.	UHL	Paul Uhlich & Co., Inc.

[a] In 1979 duPont sold its textile dye operations to Ciba-Geigy Corp.

Table 8

1979 PRODUCERS OF DIPHENYLMETHANE AND TRIARYLMETHANE DYES AND PIGMENTS

C.I. No.	C.I. Name
American Cyanamid Co.	
41000	Basic Yellow 2
41001	Basic Yellow 37
42000	Basic Green 4
42000:1	Solvent Green 1
42000:2	Pigment Green 4, PTA[a]
42040:1/ 49005:1[b]	Pigment Green 2, PTA[a]
42535	Basic Violet 1
42535:1	Solvent Violet 8
42535:2	Pigment Violet 3, fugitive[c]
42535:2	Pigment Violet 3, PTA[a]
42775	Solvent Blue 3
Atlantic Chemical Corp.	
42735	Acid Blue 104
BASF Wyandotte Corp.	
42000	Basic Green 4
42025	Basic Blue 1
42090	Acid Blue 9
42535	Basic Violet 1
42535:2	Pigment Violet 3, fugitive[c]
42535:2	Pigment Violet 3, PMA[a]
42535:2	Pigment Violet 3, PTA[a]
42600:1	Pigment Blue 14
42760	Solvent Blue 23
Buffalo Color Corp.	
42090	Food Blue 2/ Acid Blue 9[d]
42535	Basic Violet 1
Borden, Inc., Printing Ink Div., Pigments Div.	
42090:1	Pigment Blue 24
Binney and Smith, Inc.	
42595:2	Pigment Blue 1, PMA[a]
Ciba-Geigy Corp.	
42595:2	Pigment Blue 1, PMA[a]
Dye Specialties, Inc.	
42000	Basic Green 4
42000:1	Solvent Green 1
42025	Basic Blue 1
≈42025[f]	Basic Blue 2
42040	Basic Green 1
42140	Basic Blue 5
42535	Basic Violet 1
42535:1	Solvent Violet 8
42555	Basic Violet 3
42555:1	Solvent Violet 9
42595	Basic Blue 7
42595:1	Solvent Blue 5
42600	Basic Violet 4
44045	Basic Blue 26
44045:1	Solvent Blue 4

Table 8 (Continued)

C.I. No.	C.I. Name
E. I. duPont de Nemours & Co., Inc.[e]	
42535:2	Pigment Violet 3, PMA[a]
42555	Basic Violet 3
42595	Basic Blue 7
42600:1	Pigment Blue 14
44045:1	Solvent Blue 4
Keystone Color Works, Inc.	
42510:2	Pigment Violet 4
42535:2	Pigment Violet 3, fugitive[c]
H. Kohnstamm & Co., Inc.	
42040:1	Pigment Green 1
42040:1/ 49005:1[b]	Pigment Green 2, PMA[a]
42040:1/ 49005:1[b]	Pigment Green 2, PTA[a]
42090	Food Blue 2/ Acid Blue 9[d]
42090:1	Pigment Blue 24
42535:2	Pigment Violet 3, fugitive[c]
42535:2	Pigment Violet 3, PMA[a]
42535:2	Pigment Violet 3, PTA[a]
42595:2	Pigment Blue 1, PMA[a]
C. Lever Co., Inc.	
41000	Basic Yellow 2
42025:1	Pigment Blue 9
42040:1	Pigment Green 1
42090	Acid Blue 9
42600:1	Pigment Blue 14
44045:2	Pigment Blue 2

C.I. No.	C.I. Name
Magruder Color Co., Inc.	
42535:2	Pigment Violet 3, fugitive[c]
42535:2	Pigment Violet 3, PMA[a]
42595:2	Pigment Blue 1, PMA[a]
Max Marx Color & Chemical Co.	
42000:2	Pigment Green 4, fugitive[c]
42040:1	Pigment Green 1
42040:1/ 49005:1[b]	Pigment Green 2, PMA[a]
42040:1/ 49005:1[b]	Pigment Green 2, PTA[a]
42535:2	Pigment Violet 3, PMA[a]
42535:2	Pigment Violet 3, PTA[a]
42595:2	Pigment Blue 1, PMA[a]
42595:2	Pigment Blue 1, PTA[a]
Sterling Drug, Inc., Hilton Davis Chemical Co. Div.	
42025	Basic Blue 1
42080	Acid Blue 7
42090	Acid Blue 9
42090:1	Pigment Blue 24
42535:2	Pigment Violet 3, PMA[a]
42555	Basic Violet 3
42595	Basic Blue 7
42595:2	Pigment Blue 1, PTA[a]
42640	Acid Violet 49
44040	Basic Blue 11
44040:2	Pigment Blue 10
44045	Basic Blue 26
44045:1	Solvent Blue 4

Table 8 (Concluded)

C.I. No.	C.I. Name
Sherwin-Williams Co.	
42750:1	Pigment Blue 19
42775	Solvent Blue 3
Toms River Chemical Corp.	
42085	Acid Green 3
42640	Acid Violet 49
44025	Acid Green 16
Paul Uhlich & Co., Inc.	
42000:2	Pigment Green 4, fugitive[c]
42040:1	Pigment Green 1
42040:1/ 49005:1[b]	Pigment Green 2, fugitive[c]
Paul Uhlich & Co., Inc. (Continued)	
42040:1/ 49005:1[b]	Pigment Green 2, PMA[a]
42040:1/ 49005:1[b]	Pigment Green 2, PTA[a]
42535:2	Pigment Violet 3, fugitive[c]
42535:2	Pigment Violet 3, PMA[a]
42535:2	Pigment Violet 3, PTA[a]
42595:2	Pigment Blue 1, PMA[a]
Werner-Jenkinson Co.	
42053	Food Green 3
42090	Food Blue 2/Acid Blue 9[d]
42090	Acid Blue 9
42095	Acid Green 5

[a]The permanent basic dye pigments are produced by the precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA), phosphomolybdic acid (PMA), and phosphotungstomolybdic acid (PTMA).

[b]C.I. Pigment Green 2 is composed of the triphenylmethane pigment C.I. 42040:1 (C.I. Pigment Green 1) and the thiazole pigment C.I. 49005:1 (C.I. Pigment Yellow 18).

[c]The fugitive or nonpermanent pigments based on cationic dyes are usually precipitated with tannic acid or tartar emetic (antimony potassium tartrate), or with synthetic organic precipitants. Sometimes clay, fatty acids, or rosin soaps are used as precipitants.

[d]The dye C.I. 42090 is known as C.I. Food Blue 2 and C.I. Acid Blue 9. Some manufacturers producing C.I. Food Blue 2 also market it as the dye C.I. Acid Blue 9. Some manufacturers produce only the dye of a quality to be marketed as the C.I. Acid Blue 9.

[e]In 1979 duPont sold its textile dye operations to Ciba-Geigy Corp.

[f]According to Colour Index, C.I. Basic Blue 2 is "very similar" to C.I. 42025.

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